



## Dried chitosan-gels as organocatalysts for the production of biomass-derived platform chemicals

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### ABSTRACT

Aldol condensations between sugar-derived dehydrated aldehydes (e.g. furfural) and acetone have been proposed as a route to provide useful biomass-derived chemicals. In the quest of sustainable catalytic ways for such aldol condensations, this paper assesses the use of dried chitosan-gels as naturally-immobilized, readily available and non-hazardous amino-based organocatalysts. At room temperature chitosan dried gels are not suitable catalysts for the desired reaction. However, at higher temperatures (>90 °C) reaction proceeds efficiently either in solvent-free systems (with addition of catalytic amounts of water) or in water. The set-up of closed reactor set-ups (thermoshakers or microwave reactions) proved highly beneficial for the reaction outcome. Furthermore, chitosan dried gels were successfully re-used for a number of cycles. An efficient catalyst drying method (either lyophilization or scCO<sub>2</sub> drying) was crucial to achieve virtually full conversions in 4 h. After pertinent further process optimization, dried chitosan-gels may become very useful catalysts for their use in biomass-based reactions in biorefineries.

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### 1. Introduction

The production of chemicals, biofuels and commodities from biomass is currently an increasingly important research topic, involving interdisciplinary fields from biology to chemistry and chemical engineering [1–4]. Among platform chemicals obtained from biomass, furfural and 5-hydroxymethylfurfural are key structures that can be achieved from the dehydration of the sugar fractions (hemicellulose and cellulose, xylose and glucose, respectively) of lignocellulosic materials [5,6]. In this respect, lignocellulose treatment usually involves fractionation processes – the so-called pre-treatment – aiming to separate the main wood components (lignin, hemicellulose and cellulose) [3,4,7–9]. Later on processes often undergo polysaccharide depolymerizations to afford fermentable sugars [10,11], and eventually sugar dehydrations to afford aromatic aldehydes, e.g. furfural from xylose dehydration [12]. Formed furfural can be subsequently condensed with acetone, actually another chemical accessible by fermentation [13], and obtained condensates can be further hydrogenated to

form biomass-derived chemicals (e.g. alcohols, solvents, etc.), and gasoline-like alkanes (Scheme 1) [14–16]. Likewise, fermentative strategies for the production of analogous alkane-like chemicals have been put forward as well, starting from sugars (often glucose) as carbon source [13,17].

The above-described condensation route may be easily approached by classic base catalysis (e.g. NaOH). Yet, that option would lead to the production of significant amounts of wastewater at large scale. To circumvent this, several organocatalytic routes have been proposed, ranging from catalysis based on small organic molecules (e.g. proline) [18], to immobilized piperazines [19]. In this context, envisaging a huge biomass-processing load at practical scale, the quest of readily worldwide available, non-hazardous and biodegradable catalysts would certainly be privileged. With these considerations in mind, the focus of this work was put on chitosan – a common waste stream from food industry – as a naturally heterogeneous, immobilized organocatalyst. Several applications of chitosan for the aldol-like C–C bond forming reactions have been recently published [20–25]. In one of these publications, the condensation of furfural with acetone at room temperature with excellent conversions was reported by using chitosan gels [22]. Yet, very recently it was shown that these good results were actually related to the presence of NaOH impurities which were introduced

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